

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

APPLICATION FOR UNITED STATES LETTERS PATENT

for

FISCHER-TROPSCH TAIL-GAS UTILIZATION

by

Lalit Shah , Pradeep S. Thacker, Manual E. Quintana, and Rae Song

EXPRESS MAIL MAILING LABEL

NUMBER EL521284275US

DATE OF DEPOSIT October 23, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "EXPRESS MAIL POST OFFICE TO ADDRESSEE" service under 37 C.F.R. 1.10 on the date indicated above and is addressed to: Assistant Commissioner for Patents, Washington D.C. 20231.



Signature

BACKGROUND OF THE INVENTION

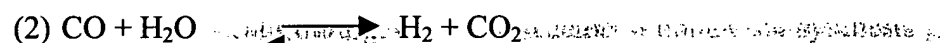
The process and advantages of gasifying hydrocarbonaceous material into synthesis gas are generally known in the industry. In high temperature gasification processes, synthesis gas is commonly produced from gaseous combustible fuels, such as natural gas and/or associated gas, liquid organic fuels or combustible solid organic fuels, such as coal, residual petroleum, wood, tar sand, shale oil, and municipal, agriculture or industrial waste. The gaseous or liquid or solid combustible organic fuels are reacted with a reactive oxygen-containing gas, such as air, enriched air, or pure oxygen, and a temperature modifier, such as steam, in a gasification reactor to obtain the synthesis gas in a oxygen deficient environment.

In the reaction zone of a gasification reactor, the contents will commonly reach temperatures in the range of about 1,700° F (930° C) to about 3,000° F (1650° C), and more typically in the range of about 2,000° F (1100° C) to about 2,800° F (1540° C). Pressure will typically be in the range of about 1 atmosphere (100 KPa) to about 250 atmospheres (25,000 KPa), and more typically in the range of about 15 atmospheres (1500 Kpa) to about 150 atmospheres (1500 KPa).

In a typical gasification process, the synthesis gas will substantially comprise hydrogen (H₂), carbon monoxide (CO), and lessor quantities of impurities, such as water (H₂O), carbon dioxide (CO₂), carbonyl sulfide (COS) and hydrogen sulfide (H₂S). The synthesis gas is commonly treated to remove or significantly reduce the quantity of impurities, particularly H₂S, COS, and CO₂ before being utilized in downstream processes. A number of acid gas removal systems are commercially available and are known in the art. Selection of an appropriate acid gas removal system will usually depend on the degree of sulfur compounds and carbon dioxide removal required and by the operating pressure of the acid gas removal system. Determinations as to what type of acid gas system to use can easily be determined by one skilled in the art of acid gas removal from syngas.

It is well known in the art that synthesis gas, also commonly referred to as syngas, can be converted to hydrocarbons in the presence of a variety of transition metal catalysts. Such metals are commonly called Fischer-Tropsch catalysts, and are known to catalyze the conversion of CO and H₂ to hydrocarbons. Common catalysts are cobalt and

iron on an alumina support. Other Group VIII metals such as ruthenium and osmium are also active. Other single metals that have been investigated as catalysts include rhenium, molybdenum, and chromium. The activities of these catalysts are commonly enhanced by the addition of a variety of metals, including copper, cerium, rhenium, manganese, platinum, iridium, rhodium, molybdenum, tungsten, ruthenium or zirconium, among others. The general chemistry of the much studied Fischer-Tropsch synthesis is as follows:



The types and amounts of reaction products obtained via Fischer-Tropsch synthesis varies upon many conditions, such as reactor type, process conditions, and type of Fischer-Tropsch synthesis catalyst used. There are four main types of F-T reactors being used commercially: tubular fixed bed reactors, entrained bed reactors, fixed-fluidized bed reactors and slurry bubble column reactors. These reactors can operate in both high and low temperature Fischer Tropsch processes. There are generally two types of Fischer Tropsch synthesis catalysts, cobalt based and iron based catalysts. Typical products of the Fischer-Tropsch reaction include hydrocarbons from C₁ to C₂₀₀ or higher, with the bulk of the hydrocarbons product being in the C₁ to C₅₀ range with chain limiting catalyst. Most of the hydrocarbons produced are mixtures of olefins and paraffins. The Fischer-Tropsch reaction also produces varying amounts of carbon dioxide, water, and oxygenated components, including acids such as acetic acid, formic acid, propionic acid; alcohols such as methyl alcohol, ethyl alcohol, propyl alcohol, and longer chained alcohols; aldehydes, ketones and esters. Typically, these oxygenated components comprise 1 to 20 weight percent of the Fischer-Tropsch reaction product, and because of their water-soluble nature are commonly found in the wastewater product of a Fischer-Tropsch reactor. Some of the oxygenated compounds are also found in hydrocarbon phase. The amount of gaseous hydrocarbons, paraffin, olefins, CO₂, oxygenates, liquid hydrocarbons, water, etc. depends on the type of reactor, catalyst employed and process conditions. For example, iron catalysts generally produce longer chain hydrocarbons that are more olefinic, produce less amount of water, higher amounts of oxygenates and higher amounts of CO₂ as compared to cobalt catalyst. The Fischer-Tropsch reaction

1 products are commonly divided into separate streams of tail-gas, liquid hydrocarbons,
2 and wastewater.

3 The product from a Fischer-Tropsch reactor typically comprise water vapor, CO₂,
4 N₂, unreacted syngas (H₂ and CO), gaseous hydrocarbons (C₁ –C₅), liquid hydrocarbon
5 (C₅+) products, and various oxygenates. Generally, most of the water vapor, liquid
6 hydrocarbon products and oxygenates are condensed and separated. This leaves the
7 desired liquid hydrocarbon product and the oxygenate containing wastewater. The liquid
8 hydrocarbon is processed in downstream product upgrading section and waste water is
9 usually sent to a water treatment step.

10 What remains is the tail-gas, which is comprised of water vapor, CO₂, CH₄, N₂,
11 unreacted syngas (H₂ and CO), and vapor hydrocarbon products. The F-T tail gas can be
12 recycled back to the gasification unit or can be recycled to the Fischer-Tropsch reactor
13 inlet or burned as fuel.

14 Electric power can be generated efficiently in integrated gasification combined
15 cycle (IGCC) systems. For IGCC applications, the synthesis gas is fired as fuel to a gas
16 turbine system that drives a generator to produce electric power. Hot turbine exhaust can
17 be passed to a heat recovery system to produce high pressure steam which can be
18 expanded through a steam turbine to drive another electric generator to produce
19 additional power. Such IGCC systems generate electricity in an efficient and
20 environmentally sound manner.

21 The production of chemicals or liquid fuels from a portion of the synthesis gas,
22 such as in a Fischer-Tropsch reactor, in a IGCC system is also well known and has the
23 advantages of common operating facilities and economy of scale in the coproduction of
24 electric power and chemicals. Several references in the background art describe existing
25 technology for combined chemical plant/IGCC power plant operations.

26 SUMMARY OF THE INVENTION

27 The present invention deals with the handling of the tail-gas product from a
28 combined gasification and Fischer-Tropsch plant. There are three major alternatives for
29 the tail-gas, the first being recycling the tail-gas as additional feed to the gasification unit.
30 The second alternative is processing the tail-gas in a CO₂ removal unit and then recycling
31 the tail-gas back to the feed of the Fischer-Tropsch reactor to improve the liquid product

1 yield. Finally, the third alternative is to send the tail-gas to a power production unit for
2 the generation of electric power.

3 BRIEF DESCRIPTION OF THE DRAWINGS

4 FIG. 1 is a schematic diagram of one embodiment of the present invention.

5 DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

6 . The feedstock for a gasification process is usually a hydrocarbonaceous material,
7 that is, one or more materials, generally organic, which provide a source of hydrogen and
8 carbon for the gasification reaction. In the present invention, carbonaceous fuel is
9 obtained and prepared for feeding to a gasification reactor. Carbonaceous fuel is any
10 solid, liquid, and gaseous combustible organic material as single feed or combinations
11 feed that can be used as feedstock to a gasification process for synthesis gas production.

12 The extent of feed preparation step will vary depending on the composition and
13 physical nature of the feedstock. Generally, solid carbonaceous fuels will need to be
14 liquefied with oil or water prior to feeding to the gasifier. Liquid and gaseous
15 carbonaceous fuels may be suitable for direct feed to the gasifier, but can be pre-treated
16 for removal of any impurities that might be present in the feed.

17 After the feed preparation step, the carbonaceous fuel is sent to a gasification
18 reactor, or gasifier. In the gasifier, the carbonaceous fuel is reacted in an oxygen
19 deficient environment with a reactive oxygen-containing gas, such as air or substantially
20 pure oxygen having greater than about 90 mole percent oxygen, or oxygen enriched air
21 having greater than about 21 mole percent oxygen. Substantially pure oxygen as
22 produced in an air separation unit or produced by membrane technology is preferred.
23 The partial oxidation of the hydrocarbonaceous material is completed, advantageously in
24 the presence of a temperature control moderator such as steam, in a gasification zone to
25 obtain hot synthesis gas.

26 In the gasification zone of a gasifier, the contents will commonly reach
27 temperatures in the range of about 1,700° F (927° C) to 3,000° F (1649° C), and more
28 typically in the range of about 2,000° F (1093° C) to 2,800° F (1538° C). Pressure will
29 typically be in the range of about 1 atmospheres (101 kPa) to about 250 atmospheres
30 (25331 kPa), and more typically in the range of about 15 atmospheres (1520 kPa) to
31 about 150 atmospheres (15,199 kPa), and even more typically in the range of about 40

1 atmospheres (6080 kPa) to about 80 atmospheres (8106 kPa). See US Patent 3,945,942
2 describing a partial oxidation burner assembly. See US Patent 5,656,044 describing a
3 method and an apparatus for the gasification of organic materials. See also US Patents
4 5,435,940, 4,851,013, and 4,159,238 describing a few of the many gasification processes
5 known in the prior art. The entire disclosures of the above referenced patents are hereby
6 incorporated by reference and relied upon.

7 The hot gasification process product, synthesis gas, or syngas, comprises carbon
8 monoxide and hydrogen. Carbon Monoxide is used as a major building block for many
9 chemicals. Hydrogen is a commercially important reactant for hydrogenation reactions.
10 Other materials often found in the synthesis gas include hydrogen sulfide, carbonyl
11 sulfide, carbon dioxide, ammonia, cyanides, and particulates in the form of carbon and
12 trace metals. The extent of the contaminants in the syngas is determined by the type of
13 carbonaceous feed, the type of gasifier, and the gasifier operating conditions. In any
14 event, the removal of these contaminants is critical to make gasification a viable process.
15 Hydrogen sulfide, removal is particularly important.

16 As the product gas is discharged from the gasifier, it is usually subjected to a
17 cooling and cleaning operation involving a scrubbing technique. The syngas from the
18 gasifier is first introduced into a scrubber and contacted with a water spray which not
19 only cools the gas but also removes particulate and ionic constituents from the synthesis
20 gas. After removing the particulates and cooling the syngas, the cooled gas is then
21 treated to desulfurize the gas prior to utilization of the synthesis gas.

22 The synthesis gas acid gas removal facilities using either amine or physical
23 solvents, removes the acid gases, particularly hydrogen sulfide. The acid gas removal
24 facilities typically operate at lower temperatures. After the synthesis gas is cooled to
25 below about 130° C, preferably below about 90° C, the contaminants in the gas,
26 especially sulfur compounds and acid gases, can be readily removed. The synthesis gas is
27 contacted with the solvent in an acid gas removal contactor. Said contactor may be of
28 any type known to the art, including trays or a packed column. Operation of such an acid
29 removal contactor is well known in the art. The cleaned syngas can be used for many
30 downstream processing. The degree of acid gas removal varies with the downstream use
31 of syngas. The recovered acid gases are sent to various recovery processes.

1
2 After being processed in the acid gas removal step, the syngas is sent to a
3 hydrocarbon synthesis reactor, such as a Fischer-Tropsch reactor, where it is contacted
4 with a hydrocarbon synthesis catalyst. Hydrocarbon synthesis catalyst converts synthesis
5 gas into hydrocarbon products. Common catalysts are cobalt and iron on an alumina
6 support. Other Group VIII metals such as ruthenium and osmium are also active. Other
7 single metals that have been investigated as catalysts include rhenium, molybdenum, and
8 chromium. The activities of these catalysts are commonly enhanced by the addition of a
9 variety of metals, including copper, cerium, rhenium, manganese, platinum, iridium,
10 rhodium, molybdenum, tungsten, ruthenium or zirconium. Many other metals can be
11 used, and it is within the scope of this invention to include all catalysts that convert
12 synthesis gas in to hydrocarbon products. See US Patents 5,780,391, 5,162,284,
13 5,102,581, 4,801,573, and 4,686,238 for illustrations of some of the various types of
14 catalyst that can be used to produce hydrocarbons from synthesis gas. The entire
15 disclosures of the above referenced patents are hereby incorporated by reference and
16 relied upon. The wide range of catalysts and catalyst modifications disclosed in the art
17 directly correspond to an equally wide range of conversion conditions in the hydrocarbon
18 synthesis reactor. Catalyst selection can provide some flexibility toward obtaining
19 selected types of products, and some control over their molecular weight distribution.

20 The types and amounts of reaction products obtained via Fischer-Tropsch
21 synthesis varies upon many conditions, such as reactor type, process conditions, and type
22 of Fischer-Tropsch synthesis catalyst used. There are four main types of F-T reactors
23 being used commercially: tubular fixed bed reactors, entrained bed reactors, fixed-
24 fluidized bed reactors and slurry bubble column reactors. These reactors can operate in
25 both high and low temperature Fischer Tropsch processes. There are generally two types
26 of Fischer Tropsch synthesis catalysts, cobalt based and iron based catalysts. Typical
27 products of the Fischer-Tropsch reaction include hydrocarbons from C₁ to C₂₀₀ or higher,
28 with the bulk of the hydrocarbons product being in the C₁ to C₅₀ range with chain limiting
29 catalyst. Most of the hydrocarbons produced are mixtures of olefins and paraffins. The
30 Fischer-Tropsch reaction also produces varying amounts of carbon dioxide, water, and
31 oxygenated components, including acids such as acetic acid, formic acid, propionic acid;

1 alcohols such as methyl alcohol, ethyl alcohol, propyl alcohol, and longer chained
2 alcohols; aldehydes, ketones and esters. Typically, these oxygenated components
3 comprise 1 to 20 weight percent of the Fischer-Tropsch reaction product, and because of
4 their water-soluble nature are commonly found in the wastewater product of a Fischer-
5 Tropsch reactor. Some of the oxygenated compounds are also found in hydrocarbon
6 phase. The amount of gaseous hydrocarbons, paraffin, olefins, CO₂, oxygenates, liquid
7 hydrocarbons, water, etc. depends on the type of reactor, catalyst employed and process
8 conditions. For example, iron catalysts generally produce longer chain hydrocarbons that
9 are more olefinic, produce less amount of water, higher amounts of oxygenates and
10 higher amounts of CO₂ as compared to cobalt catalyst. The Fischer-Tropsch reaction
11 products are commonly divided into separate streams of tail-gas, liquid hydrocarbons,
12 and wastewater.

13 The Fischer-Tropsch liquid hydrocarbon stream (light and heavy) is the desired
14 product of the hydrocarbon synthesis reactor system. This stream comprises any
15 condensed hydrocarbons that have been separated from the condensed wastewater stream
16 or removed directly from the reactor. This stream typically includes hydrocarbons chains
17 from C₅ to C₂₀₀ or higher.

18 The Fischer-Tropsch liquid wastewater stream is the water product of the
19 hydrocarbon synthesis reactor system that has been condensed and separated from the
20 light Fischer-Tropsch liquids. This wastewater stream is usually comprised of water and
21 the water soluble oxygenated components such as acids, alcohols, aldehydes, ketones and
22 esters. Small amounts of hydrocarbons can also be found in the wastewater stream,
23 subject to their solubility at the temperatures and pressures at which the condensation
24 takes place. This wastewater stream is normally passed to a water treatment facility
25 where it undergoes typical water treatment steps known in the art, such as anaerobic
26 digestion and biological oxidation, in order to remove the contaminants and produce
27 clean water for disposal or use.

28 The Fischer-Tropsch tail-gas stream is the gaseous product of a Fischer-Tropsch
29 reactor that does not condense when the reaction products are cooled. The tail-gas is
30 typically comprised of unconverted syngas and uncondensed products, typically CO, H₂,

1 CO₂, gaseous hydrocarbons (C₁-C₅), H₂O, N₂, Ar, and, depending on the catalyst, other
2 compounds and hydrocarbons.

3 Water is known to be a powerful inhibitor in the Fischer-Tropsch synthesis.
4 Carbon dioxide is also an inhibitor, but very much weaker than water. This is why it is
5 desirable to remove CO₂ from the syngas prior to processing in a Fischer-Tropsch
6 reactor. Water is generally produced by the primary step in the conversion process from
7 equation (1) above, but for iron catalyst much of the water is consumed by the reversible
8 water gas shift reaction from equation (2) above. For cobalt catalyst the reverse water

9 gas shift is not predominant. Thus, regardless of whether the selected hydrocarbon
10 synthesis catalyst produces primarily H₂O, from equation (1), or CO₂, from equation (2),
11 CO₂ is usually a significant component of the tail-gas. Generally, depending on the
12 conversion of the syngas obtained in the Fischer Tropsch synthesis, the tail gas also
13 contains large amounts of unconverted syngas. Typically, the tail-gas is recycled back to
14 the syngas feed stream to the Fischer-Tropsch reactor to improve the liquid product yield.

15 Depending on the Fischer-Tropsch catalyst employed, the tail-gas may also
16 contain varying amounts of hydrocarbons. Recycling the tail-gas back to the gasifier can
17 then convert these hydrocarbons into syngas, thus producing another step to increase the
18 overall yield of the desired Fischer-Tropsch liquid hydrocarbon product.

19 Recycling the tail-gas to the gasifier and/or to the Fischer-Tropsch reactor
20 increases the conversion to Fischer-Tropsch liquid hydrocarbons. However, the cost of
21 the related and downstream equipment also increases. Therefore, a third alternative for
22 the tail-gas, namely power generation, may also provide an economic alternative to
23 recycling the tail-gas back into the integrated gasification/Fischer-Tropsch process. The
24 tail-gas is combusted and the combusted gas is used to produce power directly by
25 expanding the combusted gas through a gas turbine, or indirectly by generation of steam
26 and expansion of that steam through a turbine. Commonly, the gasifier syngas product is
27 used in this manner for power production. It is possible that if a fraction of syngas is
28 used for power generation and fraction used for Fischer Tropsch synthesis, the syngas
29 and the tail-gas could be combined with it prior to combustion in the gas turbine. For gas
30 turbine, the BTU value and the composition of the feedgas are key parameters for
31 determining if sending the tail-gas to a gas turbine is a viable alternative. This alternative

1 is also influenced by the amount of tail-gas that is recycled to the gasifier and/or the
2 Fischer-Tropsch reactor.

3 Thus, the tail-gas could be individually recycled to the gasifier or the Fischer-
4 Tropsch reactor or sent to the gas turbine. Otherwise, the tail-gas could be sent in some
5 combination, and the flow split to two alternatives, or to all three alternatives. The
6 specifics of each project such as the catalyst used, feedstock used, the price of power, the
7 price and desired composition of the Fischer-Tropsch liquids, and the price of the
8 carbonaceous feedstock are all items to be considered in determining the optimum
9 arrangement for tail-gas utilization.

10 Referring now to FIG. 1, solid carbonaceous fuel 2 and water 4 are sent to a slurry
11 preparation step 6 to produce liquefied solid carbonaceous feedstock 8. For the gaseous
12 and liquid feed slurry preparation step 6 will not be necessary and feedstock 8 will be the
13 gaseous or liquid feed. The feedstock 8 is then sent to gasifier 10, along with oxygen 14,
14 usually from an air separation unit 12, and steam 16, used as a temperature moderator.
15 At least a portion 42 of the tail-gas product 32 or the entire tail gas stream 32 from the
16 downstream Fischer-Tropsch reactor 28 is also sent to the gasifier 10. The gasifier 10
17 syngas product 18 is then sent to acid gas unit 20, where a substantial portion of the
18 impurities of the syngas 18 are removed. A portion of the sweetened syngas 22 can then
19 be sent to power block 24, where it is likely to be combusted and expanded across a
20 turbine to generate power, and/or is used to produce steam that can also be used to
21 generate power. It is possible that all of the syngas from the acid gas removal unit 20 is
22 sent to the Fischer Tropsch unit. Hence either some or all of the portion of the
23 sweetened syngas 26 is sent to Fischer-Tropsch reactor 28, where it is reacted with a
24 catalyst to form wastewater 29, liquid synthetic hydrocarbons 30, and tail-gas 32. There
25 are two alternates with tail gas 32. One alternate is to process tail gas through the second
26 acid gas removal unit to remove CO₂. The second alternate is to send tail-gas as it is
27 without CO₂ removal. In the first alternate the tail-gas 32 is processed in a second acid
28 gas unit 34, where a substantial portion of the CO₂ present in the tail-gas 32 is removed.
29 The sweetened tail-gas 36 can then be divided among three options: 1) recycled 38 back
30 to the Fischer-Tropsch reactor 28 for additional hydrocarbon synthesis; 2) sent to the
31 power block 24 for additional power generation; and at least 3) recycled back to the

1 gasifier 10 for additional syngas production. In the second alternate the tail-gas 32 can be
2 divided among two options: 1) recycled 46 directly to the gasifier 10 for additional
3 syngas production; and 2) recycled 44 to the power block 24 for additional power
4 generation. Each of the above options are viable as whole or in combinations with other.

5 While the devices, compositions and methods of this invention have been
6 described in terms of preferred embodiments, it will be apparent to those of skill in the art
7 that variations may be applied to the process described herein without departing from the
8 concept and scope of the invention. All such similar substitutes and modifications
9 apparent to those skilled in the art are deemed to be within the scope and concept of the
10 invention as it is set out in the following claims.

11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000
1001
1002
1003
1004
1005
1006
1007
1008
1009
1010
1011
1012
1013
1014
1015
1016
1017
1018
1019
1020
1021
1022
1023
1024
1025
1026
1027
1028
1029
1030
1031
1032
1033
1034
1035
1036
1037
1038
1039
1040
1041
1042
1043
1044
1045
1046
1047
1048
1049
1050
1051
1052
1053
1054
1055
1056
1057
1058
1059
1060
1061
1062
1063
1064
1065
1066
1067
1068
1069
1070
1071
1072
1073
1074
1075
1076
1077
1078
1079
1080
1081
1082
1083
1084
1085
1086
1087
1088
1089
1090
1091
1092
1093
1094
1095
1096
1097
1098
1099
1100
1101
1102
1103
1104
1105
1106
1107
1108
1109
1110
1111
1112
1113
1114
1115
1116
1117
1118
1119
1120
1121
1122
1123
1124
1125
1126
1127
1128
1129
1130
1131
1132
1133
1134
1135
1136
1137
1138
1139
1140
1141
1142
1143
1144
1145
1146
1147
1148
1149
1150
1151
1152
1153
1154
1155
1156
1157
1158
1159
1160
1161
1162
1163
1164
1165
1166
1167
1168
1169
1170
1171
1172
1173
1174
1175
1176
1177
1178
1179
1180
1181
1182
1183
1184
1185
1186
1187
1188
1189
1190
1191
1192
1193
1194
1195
1196
1197
1198
1199
1200
1201
1202
1203
1204
1205
1206
1207
1208
1209
1210
1211
1212
1213
1214
1215
1216
1217
1218
1219
1220
1221
1222
1223
1224
1225
1226
1227
1228
1229
1230
1231
1232
1233
1234
1235
1236
1237
1238
1239
1240
1241
1242
1243
1244
1245
1246
1247
1248
1249
1250
1251
1252
1253
1254
1255
1256
1257
1258
1259
1260
1261
1262
1263
1264
1265
1266
1267
1268
1269
1270
1271
1272
1273
1274
1275
1276
1277
1278
1279
1280
1281
1282
1283
1284
1285
1286
1287
1288
1289
1290
1291
1292
1293
1294
1295
1296
1297
1298
1299
1300
1301
1302
1303
1304
1305
1306
1307
1308
1309
1310
1311
1312
1313
1314
1315
1316
1317
1318
1319
1320
1321
1322
1323
1324
1325
1326
1327
1328
1329
1330
1331
1332
1333
1334
1335
1336
1337
1338
1339
1340
1341
1342
1343
1344
1345
1346
1347
1348
1349
1350
1351
1352
1353
1354
1355
1356
1357
1358
1359
1360
1361
1362
1363
1364
1365
1366
1367
1368
1369
1370
1371
1372
1373
1374
1375
1376
1377
1378
1379
1380
1381
1382
1383
1384
1385
1386
1387
1388
1389
1390
1391
1392
1393
1394
1395
1396
1397
1398
1399
1400
1401
1402
1403
1404
1405
1406
1407
1408
1409
1410
1411
1412
1413
1414
1415
1416
1417
1418
1419
1420
1421
1422
1423
1424
1425
1426
1427
1428
1429
1430
1431
1432
1433
1434
1435
1436
1437
1438
1439
1440
1441
1442
1443
1444
1445
1446
1447
1448
1449
1450
1451
1452
1453
1454
1455
1456
1457
1458
1459
1460
1461
1462
1463
1464
1465
1466
1467
1468
1469
1470
1471
1472
1473
1474
1475
1476
1477
1478
1479
1480
1481
1482
1483
1484
1485
1486
1487
1488
1489
1490
1491
1492
1493
1494
1495
1496
1497
1498
1499
1500
1501
1502
1503
1504
1505
1506
1507
1508
1509
1510
1511
1512
1513
1514
1515
1516
1517
1518
1519
1520
1521
1522
1523
1524
1525
1526
1527
1528
1529
1530
1531
1532
1533
1534
1535
1536
1537
1538
1539
1540
1541
1542
1543
1544
1545
1546
1547
1548
1549
1550
1551
1552
1553
1554
1555
1556
1557
1558
1559
1560
1561
1562
1563
1564
1565
1566
1567
1568
1569
1570
1571
1572
1573
1574
1575
1576
1577
1578
1579
1580
1581
1582
1583
1584
1585
1586
1587
1588
1589
1590
1591
1592
1593
1594
1595
1596
1597
1598
1599
1600
1601
1602
1603
1604
1605
1606
1607
1608
1609
1610
1611
1612
1613
1614
1615
1616
1617
1618
1619
1620
1621
1622
1623
1624
1625
1626
1627
1628
1629
1630
1631
1632
1633
1634
1635
1636
1637
1638
1639
1640
1641
1642
1643
1644
1645
1646
1647
1648
1649
1650
1651
1652
1653
1654
1655
1656
1657
1658
1659
1660
1661
1662
1663
1664
1665
1666
1667
1668
1669
1670
1671
1672
1673
1674
1675
1676
1677
1678
1679
1680
1681
1682
1683
1684
1685
1686
1687
1688
1689
1690
1691
1692
1693
1694
1695
1696
1697
1698
1699
1700
1701
1702
1703
1704
1705
1706
1707
1708
1709
1710
1711
1712
1713
1714
1715
1716
1717
1718
1719
1720
1721
1722
1723
1724
1725
1726
1727
1728
1729
1730
1731
1732
1733
1734
1735
1736
1737
1738
1739
1740
1741
1742
1743
1744
1745
1746
1747
1748
1749
1750
1751
1752
1753
1754
1755
1756
1757
1758
1759
1760
1761
1762
1763
1764
1765
1766
1767
1768
1769
1770
1771
1772
1773
1774
1775
1776
1777
1778
1779
1780
1781
1782
1783
1784
1785
1786
1787
1788
1789
1790
1791
1792
1793
1794
1795
1796
1797
1798
1799
1800
1801
1802
1803
1804
1805
1806
1807
1808
1809
1810
1811
1812
1813
1814
1815
1816
1817
1818
1819
1820
1821
1822
1823
1824
1825
1826
1827
1828
1829
1830
1831
1832
1833
1834
1835
1836
1837
1838
1839
1840
1841
1842
1843
1844
1845
1846
1847
1848
1849
1850
1851
1852
1853
1854
1855
1856
1857
1858
1859
1860
1861
1862
1863
1864
1865
1866
1867
1868
1869
1870
1871
1872
1873
1874
1875
1876
1877
1878
1879
1880
1881
1882
1883
1884
1885
1886
1887
1888
1889
1890
1891
1892
1893
1894
1895
1896
1897
1898
1899
1900
1901
1902
1903
1904
1905
1906
1907
1908
1909
1910
1911
1912
1913
1914
1915
1916
1917
1918
1919
1920
1921
1922
1923
1924
1925
1926
1927
1928
1929
1930
1931
1932
1933
1934
1935
1936
1937
1938
1939
1940
1941
1942
1943
1944
1945
1946
1947
1948
1949
1950
1951
1952
1953
1954
1955
1956
1957
1958
1959
1960
1961
1962
1963
1964
1965
1966
1967
1968
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
1984
1985
1986
1987
1988
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
2024
2025
2026
2027
2028
2029
2030
2031
2032
2033
2034
2035
2036
2037
2038
2039
2040
2041
2042
2043
2044
2045
2046
2047
2048
2049
2050
2051
2052
2053
2054
2055
2056
2057
2058
2059
2060
2061
2062
2063
2064
2065
2066
2067
2068
2069
2070
2071
2072
2073
2074
2075
2076
2077
2078
2079
2080
2081
2082
2083
2084
2085
2086
2087
2088
2089
2090
2091
2092
2093
2094
2095
2096
2097
2098
2099
2100
2101
2102
2103
2104
2105
2106
2107
2108
2109
2110
2111
2112
2113
2114
2115
2116
2117
2118
2119
2120
2121
2122
2123
2124
2125
2126
2127
2128
2129
2130
2131
2132
2133
2134
2135
2136
2137
2138
2139
2140
2141
2142
2143
2144
2145
2146
2147
2148
2149
2150
2151
2152
2153
2154
2155
2156
2157
2158
2159
2160
2161
2162
2163
2164
2165
2166
2167
2168
2169
2170
2171
2172
2173
2174
2175
2176
2177
2178
2179
2180
2181
2182
2183
2184
2185
2186
2187
2188
2189
2190
2191
2192
2193
2194
2195
2196
2197
2198
2199
2200
2201
2202
2203
2204
2205
220